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(54) **Process for the preparation of polymer powder using supercritical fluid**

Verfahren zur Herstellung von Polymerpulver unter Verwendung von superkritischer Flüssigkeit

Procédé de fabrication d'une poudre de polymère utilisant un fluide supercritique

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(56) References cited:

EP-A- 0 136 813	EP-A- 0 220 603
EP-A- 0 239 035	EP-A- 0 301 532
EP-A- 0 590 842	EP-A- 0 806 438
EP-A- 0 964 009	WO-A-00/05273
WO-A-01/57095	WO-A-93/20116
WO-A-96/28477	WO-A-98/28351
WO-A-98/34967	DE-A- 1 745 386
US-A- 5 506 317	US-A- 5 530 077
US-A- 5 552 502	US-A- 5 824 726
US-A- 6 057 409	

- **DATABASE WPI Section Ch, Week 199626**
Derwent Publications Ltd., London, GB; Class
A82, AN 1996-255209 XP002188945 & JP 08
104830 A (NIPPON PAINT CO LTD), 23 April 1996
(1996-04-23)
- **DATABASE WPI Section Ch, Week 200167**
Derwent Publications Ltd., London, GB; Class
A14, AN 2001-592417 XP002188946 & JP 2001
151802 A (KEIZAI SANGYOSHO SANGYO
GIJUTSU SOGO KEN), 5 June 2001 (2001-06-05)

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Description

[0001] The invention relates to a method of preparation for polymers, particularly binders for powder coatings, and powder coatings which are prepared as a solution in a supercritical fluid phase.

[0002] Processes for the preparation of polymers using solvents in the supercritical (sc) state, particularly sc CO₂, are already known in the literature. In these processes, monomers or oligomers are dissolved in supercritical solvents and then allowed to react. The resulting polymers are usually insoluble in the supercritical solvent and form two-phase systems. High molecular weights may be obtained with this method of preparation. Such processes are already described, e.g., in US 5 328 972, in which, however, only about 20 wt-% of monomers are present in sc CO₂, in EP 0 735 051, which describes a process for polymerisation in supercritical solvents in which homopolymers or copolymers of thermoplastic resins are prepared, in EP 0 220 603, in which polymers in powder form based on special unsaturated vinyl compounds are prepared in sc CO₂. In these processes which use, in principle, a large proportion of supercritical solvents, particularly CO₂, it is known that resulting polymers are no longer dissolved homogeneously in the fluid phase in the required reaction conversions. A disadvantage of reactions in this phase (emulsion polymerisation, dispersion polymerisation) in supercritical media is the use of expensive stabilisers. Moreover, problems may occur in controlling and conducting the reaction.

[0003] Moreover, processes are known in which polymers are liquefied by means of a solvent in the supercritical state, e.g., sc CO₂, under pressure and at elevated temperature, wherein hardeners and additives may optionally be introduced into the mixture in the resulting viscous phase and the mixture under pressure is then depressurised in order to obtain materials in powder form and powder coatings. Examples of such processes are described in EP 669 858, WO 99/24 493, and EP 0 744 992 in which a process for the preparation of particles and powders is described with depressurisation of a viscous mixture of the substance to be converted to a powder and a supercritical solvent.

[0004] These processes operate according to the sequence whereby the polymer or the individual components of a polymer mixture must be melted, impinged on by the supercritical solvent and homogenised and, after the optional addition of further components, the corresponding powder is obtained after a depressurisation step. A known disadvantage is that of fresh process steps of melting and homogenising the resin material with the supercritical solvent. This is associated with exposure to high temperatures which, if reactive components are used, may lead to side reactions and hence to the unusability of the material.

[0005] The object of the invention is to provide a process in which, starting from monomers capable of free-

radical or ionic polymerisation and which may be mixed homogeneously in sc fluids, a homogeneously dissolved polymer is produced and this is separated from the supercritical phase. A further object is to provide a process in which, after the polymer has been prepared, said polymer is further processed directly without leaving the supercritical phase state, and hardeners, additives and further components are added in the fluid state and the viscous/fluid mixture is then depressurised in order to obtain an uncross-linked powder coating in powder form.

[0006] It has become apparent that the object may be achieved by the process according to the invention for the preparation of binders for powder coatings from at least two ethylenically unsaturated monomers capable of free-radical or ionic copolymerisation and conventional starters and regulators in sc fluids, characterised in that

the monomers, initiators (starter) and regulators are mixed with the sc fluid to give a mixture with a sc fluid content up to 37,5 wt% before initiating the polymerisation

- polymerisation is carried out in the homogeneous phase,
- after the reaction has ended the phase parameters (pressure, temperature) of the mixture are altered so that at least two phases with supercritical fluid are obtained, a polymer phase (I) saturated with sc fluid and a second phase (II) containing substantially sc fluid and monomer, and
- the polymer phase is separated and the polymer is separated as a powder from the sc fluid by depressurisation and removing the sc fluid.

[0007] A further embodiment of the invention separates phase II monomers/sc fluid from the two supercritical phases, mixes the remaining homogeneous phase I polymer/sc fluid with further components such as additives, auxiliaries and hardeners at a temperature at which no cross-linking reactions occur, and the resulting fluid mixture is converted to a solid in powder form by depressurising the sc fluid.

[0008] A further embodiment of the invention recycles the separated phase of unreacted monomers/sc fluid to the reaction mixture for polymerisation.

[0009] A further embodiment of the invention does not depressurise the sc phase I into air but carries out depressurisation into an organic liquid or water.

[0010] The term supercritical (sc) fluids refers herein-after to gases, vapours, liquids or mixtures of these substances which, under the physical conditions applied, are in a near-critical or supercritical state and in which the monomers, additives, polymers and further components of the polymerisation reaction may be obtained homogeneously. Phases of sc fluids and monomers, polymers or further components are called sc phases. In the process according to the invention, various gases

or liquids may be used at reaction temperature as the sc fluid, e.g., carbon dioxide, dinitrogen oxide; hydrocarbons such as methane, ethane, ethylene, propane, propylene, butane, cyclohexane, toluene, benzene; ethers such as dimethyl ether, tetrahydrofuran; ketones such as acetone, methyl ethyl ketone, halogenated hydrocarbons such as CClF_3 , CH_3F ; alcohols or ammonia. More particularly, however, fluids which are non reactive under the polymerisation conditions are suitable, particularly methane, ethane, propane, butane, dinitrogen oxide, dimethyl ether and carbon dioxide; non combustible substances are more particularly preferred, particularly carbon dioxide or dinitrogen oxide. Mixtures of two or more of the components may also be used.

[0011] Examples of suitable polymerisable monomers include unsaturated monomers capable of free-radical polymerisation such as styrene, vinyltoluene, α -methylstyrene, p-methylstyrene, p-methoxystyrene, p-tert. butylstyrene; linear or branched vinyl esters of aliphatic carboxylic acids such as vinyl acetate, vinyl propionate, versatic acid vinyl ester; vinyl ethers such as methyl-, ethylvinyl ethers; (meth)acrylonitrile, (meth)acrylamide; esters and amides of α,β -unsaturated mono- or dicarboxylic acids such as crotonic acid, isocrotonic acid, itaconic acid, fumaric acid, maleic acid, tetrahydrophthalic acid, branched or unbranched alkyl (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, propyl- or isopropyl (meth)acrylate, pentyl (meth)acrylate, isomeric butyl (meth)acrylate, hexyl (meth)acrylate, isomeric octyl (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, stearyl (meth)acrylate; alicyclic C_5 to C_{12} -alkyl (meth)acrylic esters such as cyclopentyl (meth)acrylate, cyclohexyl (meth)acrylate, methylcyclohexyl (meth)acrylate, isobornyl (meth)acrylate, norbornyl (meth)acrylate, tert-butylcyclohexyl (meth)acrylate, trimethylcyclohexyl (meth)acrylate; or functionalised monomers such as glycidyl (meth)acrylate, 1,2-epoxybutyl (meth)acrylate, 2,3-epoxycyclopentyl (meth)acrylate, (meth)allyl glycidylether, 3,4-epoxy-1-vinylcyclohexane, hydroxyethyl (meth)acrylate, isomeric hydroxypropyl (meth)acrylate, butane diol monoacrylate, hydroxyhexyl acrylate, hydroxyoctyl acrylate, dialkylaminoalkyl (meth)acrylamide, isomeric hydroxybutyl (meth)acrylate; reaction products of glycidyl (meth)acrylate with acetic acid, propionic acid, butyric acid, acrylic acid, methacrylic acid, itaconic acid, crotonic acid, aconitic acid, half esters of maleic or fumaric acid, N-alkoxyalkyl (meth)acrylamide such as N-methylol (meth)acrylamide etc. Suitable copolymerisable monomers are described for example in DE 199 09 944. The corresponding monomers should be substantially ethylenically monofunctional and lead to linear polymers. In specific cases, small proportions of difunctional monomers may also be present. The monomers may be selected according to the desired properties of the polymer. If only monomers without additional functional groups are selected, uncross-linked polymers are obtained, but proportions of the monomers

should preferably contain further functional groups such as epoxy groups, OH groups, carboxyl groups etc. so that cross-linkable polymers are obtained. Depending on the choice of functionalised monomers, externally cross-linking or self-cross-linking binders may be obtained. Care should be taken to ensure that under the reaction conditions of polymerisation, a reaction with the sc fluid or with the complementary reactive group is avoided.

[0012] More particularly, it is advantageous for powder coating applications to obtain a glass transition temperature of the polymers (T_g) of $> +30^\circ\text{C}$ (determined by DSC, Differential Scanning Calorimetry), particularly $> +40^\circ\text{C}$. The T_g may be influenced by the choice of monomers. Suitable compositions are already described in the literature and may be selected and adjusted accordingly by the skilled person.

[0013] The well known radical or ionic initiators may be used as initiators for polymerisation in sc fluid. Examples of such initiators include azo compounds such as azobisisobutyronitrile (AIBN), peroxides such as benzoyl peroxide, tert-butyl hydroperoxide, tert-amyl perbenzoate, di-tert butylperoxide, peroxyformic acid or other peracids, chlorine- and fluorine-based percompounds which are soluble in the sc medium such as trichloroacetyl peroxide, bis (perfluoro-2-propoxypropyl)peroxide and H_2O_2 . It is possible to reduce the activation energy of peroxide decomposition and hence increase the rate of decomposition at low temperatures by adding reducing agents. Examples thereof include sodium hyposulfite; readily enolisable carbonyl compounds such as ascorbic acid, hydroxyacetone; metal ions such as Cu^+ , Fe^{2+} , V^{2+} , Co^{2+} ; amines such as N, N-dialkylaniline. Regulators such as Co-complexes, mercaptans, inhibitors etc, but preferably no emulsifiers are added to the mixture.

[0014] The polymers prepared by the process according to the invention comprise preferably at least three copolymerisable monomers, preferably at least one monomer containing one further reactive group which is stable under the polymerisation conditions in addition to the unsaturated group.

[0015] Optionally, it may be advantageous to add proportions of one or more organic cosolvents to the sc fluid in order to obtain improved compatibility of polymer, monomer and sc fluid. The choice should be tailored to the monomer composition. Examples thereof include ketones, such as acetone, methylisobutyl ketone, methyl ethyl ketone; alcohols such as ethanol, iso-propanol, butanol; ethers such as diethyl ether, dibutyl ether, tetrahydrofuran; esters such as butyl acetate, ethyl acetate or aromatic solvents. The cosolvents should have a low boiling point and their proportion should be max. 20 wt-% of the sc fluid, preferably max. 10%.

[0016] The monomers are mixed homogeneously with the sc fluid under the process conditions or, after mixing, converted to the supercritical homogeneous state, optionally further additives and initiators and pro-

portions of cosolvents are added and mixed homogeneously, and then polymerisation is initiated. The reaction may be initiated by elevated temperature or by other methods such as, e.g., by UV radiation or the addition of redox catalysts. The corresponding conditions are well known and selected according to the initiator used.

[0017] The sc fluid content of the mixture, e.g. preferably CO₂, is up to 37.5 wt-%, particularly up to 25 wt-%. In the event of a higher sc CO₂ content, the solubility of the polymer is low so that only a low conversion may be obtained. If the sc CO₂ content selected is too low, a substantial increase in viscosity of the reaction mixture is noticed and it is difficult to ensure an advantageous molecular weight distribution. The reaction time is from 5 to 240 minutes, particularly from 10 to 150 minutes.

[0018] The temperature and pressure of the reaction mixture should be above the critical point of the sc fluid, in the case of sc CO₂ above 31.4°C and 7.29 x 10⁶ Pa (72.9 bar). For other sc fluids, the corresponding values are described in the literature. The temperature is raised until a sufficient rate of polymerisation of the monomers is obtained, for example, from 70 to 250°C, particularly from 80 to 200°C, particularly preferably from 100 to 150°C. The pressure of the reaction mixture is above the critical pressure of the sc fluid. Optionally, it may be up to 2 x 10⁸ Pa (2000 bar), but a pressure from 8 x 10⁶ to 4.5 x 10⁷ Pa (80 to 450 bar), particularly up to 3.5 x 10⁷ Pa (350 bar) is preferred.

[0019] The number-average molecular weight (M_w) of the polymer is adjusted to 2,000 to 12,000, particularly from 3,000 to 9,000. The reaction is conducted until a homogeneous mixture of the resulting polymer in the mixture of monomers and sc fluid is ensured. The conversion may be from 25 to 100%, preferably from 40 to 95%. The reaction mixture should be homogeneous, i. e. sc fluid, optionally additional solvents, monomer mixture and polymer form one phase. The homogeneity may be ascertained by measuring turbidity, by visually monitoring the mixture, or by spectroscopic measurement. It also depends on the pressure of the reaction mixture. The reaction is ended before nonhomogeneity occurs, i.e. precipitation of the polymer, e.g., by lowering the temperature, lowering the pressure, by adding sc fluid or by a combination of these measures. The mixture is still in the sc state but nonhomogeneities may also occur after the reaction has ended. The resulting polymer has a narrow molecular weight distribution and a low dispersity D ($M_w : M_n$), generally $D < 3$, particularly $D < 2$.

[0020] After the reaction has ended, a phase separation into two sc phases in the reaction mixture is brought about. This is achieved by altering the temperature and/or altering the pressure. Further sc fluid can be added to the mixture whereby a phase separation occurs, i.e. a fluid phase I is obtained comprising predominantly polymer and sc fluid, and a further fluid phase II comprising predominantly monomers and sc fluid. The phase I with the polymers is separated. This phase still containing sc

fluid and optionally proportions of cosolvents or monomers and is further processed by depressurisation, as described above. In so doing, the cosolvents and other volatile constituents are generally also separated with the sc fluid from the polymer powder by the separation.

[0021] Optionally, it is also possible to add to the separated phase I of polymer/sc fluid, mix and optionally dissolve a quantity of sc fluid, if need be once or several times. Remaining monomers or cosolvents may be removed from the polymer by removing and depressurising the sc fluid in each case. It is also possible to extract phase I and a phase of an identical or different sc fluid continuously in the countercurrent process and thus to separate monomers and/or accompanying products.

[0022] The polymerisation reaction may be carried out batchwise or continuously. A preferred embodiment recycles the separated phase II of monomers/sc fluid to the reaction mixture, particularly in a continuous mode of operation. The consumed participants in the reaction, e.g., monomers or initiators, are made up with a corresponding aliquot, or accompanying substances are removed first from the sc fluid before re-use.

[0023] The reaction may be carried out in suitable reaction vessels, e.g., a batch reactor, a continuously operated stirred reactor, a cascade of stirred reactors, or a flow tube reactor which are provided with the necessary metering, temperature, pressure and control facilities.

[0024] After depressurisation of phase I, comprising the polymer and the sc fluid, and separating the sc fluid, the obtained polymer particles may be manufactured as powder coating compositions by well known techniques such as, e.g., the extruder process.

[0025] Other well known processes for the manufacture of powder coating compositions are e.g. the method of ultrasonic atomisation, method under assistance of sc fluids, as described e.g. in WO 99/24 493, method of steam assisted micronisation.

[0026] Further components which are suitable for use in the powder coating may be added to the polymer particle and/or during the processes. Examples of such components include hardeners, additives such as stabilisers, levelling agents, degassing agents, light stabiliser, dyes, pigments and extenders. Such substances are already described in the literature and they may be selected and added according to the given application of the powder coating.

[0027] A further, particularly preferred embodiment of the invention is that of separating the sc phase I and continuously carrying out the process for the preparation of a powder coating under supercritical process conditions and finishing in conventional manner.

[0028] The phase I/polymer/sc fluid obtained may be mixed with additional sc fluid. Further components which are suitable for use in the powder coating may be added to this mixture ("process mixture") by known methods. Examples of such components include hardeners, additives such as stabilisers, levelling agents, de-

gassing agents, light stabiliser, dyes, pigments and extenders., which are well known and which may be selected and added according to the given application of the powder coating.

[0029] These components may be metered directly into the process mixture; optionally, it is also possible to lower the viscosity of polymer components in the form of a mixture with identical or different sc fluids and then to meter them into the process mixture, as described, e. g., in WO 99/24493. Mixing may take place with inherently known devices and methods, e.g. static mixers. Further possibilities of homogenisation and particle formation include, e.g., ultrasonic sources, or a mixture may be obtained by means of a suitable flow system, e. g. by tangential flows, jet flows or impact flows. Such methods are described, for example, in WO 95/21 688 or in WO 99/24 493.

[0030] A particular embodiment adds a hardener to the process mixture which hardener may preferably also be mixed with sc fluid before being mixed with the polymers. Externally cross-linking coating systems are obtained in so doing. Hardeners for powder coating binders are already generally well known. For example, they are solid, low molecular weight or polymer compounds having two or more carboxyl groups or anhydride groups per molecule. Further examples include carboxy-functional oligo- and polyesters or oligo- and polyurethanes. The hardener component should optionally be tailored to the corresponding reactive groups of the polymer. The temperature of the mixture of hardener/polymer should be below the reaction temperature of the cross-linking reaction. The viscosity of the process mixture may be influenced by the amount of sc fluid.

[0031] The subsequent process step of depressurising the process mixture to obtain the powder coating may take place in various ways. For example, the mixture may be depressurised by means of a nozzle in a short period of time, or a time-dependent depressurisation is carried out inside a pressure vessel. Due to depressurisation, the resulting particles are cooled to below their solidification temperature and the primary particle distribution obtained during the depressurisation process remains in tact since subsequent sintering of the powders is avoided. The particle size of the powder coating particles may be influenced by a suitable choice of process parameters, e.g., pressure, temperature, flow rate, type of nozzle, diameter of nozzle, viscosity, concentration of the solution under pressure. These particles generally have a diameter from 1 to 150 μm , particle sizes below 50 μm being preferred, particularly from 10 to 30 μm .

[0032] While the sc fluid is being removed it is possible to remove further volatile constituents optionally contained in the mixture.

[0033] A further embodiment does not spray the process mixture into a gas atmosphere but atomisation takes place into a liquid phase, e.g., into an aqueous phase. Additives may optionally be contained in this liquid

phase. A preferably aqueous slurry of a powder material is thus obtained.

[0034] Variants of the way in which the process is conducted are shown diagrammatically by way of example in the drawings.

Figure 1 shows a process for the preparation of a polymer in the homogeneous phase, separation of the phases I (sc fluid/polymer) and phase II (monomers/sc fluid) and separation of the polymer powder. Figure 2 shows a process in which the process is supplemented by the additional step of adding hardeners and/or additives.

[0035] Figure 3 shows a diagram of the process in which, in addition, the process step of extraction of residual monomers and accompanying substances from phase I is carried out and the sc fluid is recycled. The product obtained in this case after further components have been added is a powder coating. V 1 means a storage vessel for sc fluid, in this case sc CO_2 and monomers, V2 means a storage vessel for hardener, optionally with sc fluid. W represents a heat exchanger for appropriate control of the process heat, R is the reactor and P1 to P5 mean pumps for conveying sc fluid or process mixture. The separator A separates two supercritical phases (polymer-rich and monomer-rich). In the static mixer M the process mixture is homogenised and in spray tower S phase I is sprayed and a polymer powder or powder coating is obtained. Z represents a cyclone for purifying the gaseous constituents which separates proportions of the product and the gaseous constituents. E represents a counter-current extraction plant for working up phase II. The sc extraction phase is recycled and monomer constituents are separated.

[0036] The product obtained is either a polymer powder or a complete powder coating if hardener and optionally further components are added to the product.

[0037] The process according to the invention may be carried out both continuously and batchwise. By means of an appropriate arrangement of equipment it is possible to avoid cost-intensive process steps such as depressurisation, pressure build-up, dissolution of the polymers or polymer-stressing steps such as heating, melting as a process step. By adding or separating sc fluid or by altering the process parameters, it is possible to influence the phase behaviour during the production process.

[0038] The polymers prepared by the process according to the invention comprise at least two, particularly three or more copolymerisable monomers, particularly preferably at least one monomer containing a further reactive group which is stable under the polymerisation conditions. As a result of the process according to the invention for preparing polymers in the homogeneous phase, a particularly favourable molecular weight distribution is obtained with a dispersity of preferably $D < 2$. Such resins are also particularly suitable as powder coating binders.

[0039] Due to the use of sc fluid, the viscosities required for conducting the reaction may be lowered so

that the polymerisation reaction may be carried out at low temperatures. This results in a mild process for the preparation of binders and polymers which may be further processed for various applications. These mixtures may be further processed as a polymer/sc fluid to powder coating without depressurisation of the sc fluid.

[0040] The powder coatings prepared according to the invention may be used, for example, as coating compounds for industrial coating where they may have decorative purposes and/or a protective effect, e.g., against corrosion. They may be used as clear coat of, if mixed e.g., with pigments or dyes, as a filler or base coat or top coat. The thickness of the coating may be from 10 to 250 μm , more particularly the coating thickness should be below 50 μm . The powder coatings prepared according to the invention are suitable for coating industrial articles, e.g., furniture, exterior wall coatings, electrical appliances and automotive parts.

Example 1 (preparation of a powder coating, continuous)

[0041] A polymer was prepared by the following process: A mixture of 15.0 g of glycidyl methacrylate, 6.6 g of methyl methacrylate, 6.6 g of iso-bornyl methacrylate, 1.8 g of styrene, 2.5 g of dodecyl mercaptan and 0.09 g of di-tert-butyl peroxide as initiator were mixed in an autoclave for 1 hour with 4.8 g of CO_2 ($T=0^\circ\text{C}$, $p=200$ bar). The mixture was transferred to a pressure-stable reaction vessel preheated to 120°C . The reaction ($T=120^\circ\text{C}$, $p=350$ bar) started with the transfer of the mixture to the reaction vessel. The reaction mixture was homogeneous. After 240 minutes, the reaction was stopped by depressurising and draining the reaction mixture from the reaction vessel.

[0042] The monomer conversion was 90 %. A solid powder was obtained. The polymer had an M_N of 2600 g/mole, an M_W of 4300 g/mole, and a polymolecularity index of 1.65. The T_g was about $30 - 50^\circ\text{C}$. The reaction mixture with polymer was separated into two fluid phases by reducing the pressure to 1.5×10^7 Pa (150 bar). A phase (I) polymer/sc fluid and a phase (II) monomer/sc fluid was obtained. Phase (II) was separated and then discarded. 20 wt-% of an anhydride hardener (Additol VXL 11381, Vianova Resins AG) and 0.5 wt-% of a commercial light stabiliser (based on a sterically hindered amine) were added to phase (I), CO_2 was added in a quantity of about 35 wt-% (based on polymer/hardener) and the mixture was homogeneously mixed in a static mixer ($T=100^\circ\text{C}$, $p=150$ bar). The viscous mixture was then depressurised by means of a high-pressure nozzle ($d=0.8$ mm) into a spray tower. The temperature in the spray tower was $35 - 40^\circ\text{C}$. A powder coating with an average particle size of about $25 \mu\text{m}$ was obtained.

Example 2

[0043] A polymer according to Example 1 was pre-

pared.

[0044] The reaction mixture with polymer was separated into two fluid phases by adding sc CO_2 (30 wt-% based on mixture): a phase (I) polymer/sc fluid and a phase (II) monomer/sc fluid. The temperature was reduced to 90°C in so doing and phase (II) was separated and then discarded. Whilst maintaining the physical conditions, 20 wt-% of an anhydride hardener (Additol VXL 11381, Vianova Resins AG) and 0.5 wt-% of a commercial light stabiliser (based on a sterically hindered amine) were added to phase (I), CO_2 was added in a quantity of about 30 wt-% (based on polymer/hardener) and the mixture was homogeneously mixed in a static mixer ($T=100^\circ\text{C}$, $p=150$ bar). The viscous mixture was then depressurised by means of a high-pressure nozzle ($d=0.8$ mm) into a spray tower. The temperature in the spray tower was $35 - 40^\circ\text{C}$. A powder coating with an average particle size of about $25 \mu\text{m}$ was obtained.

Example 3

[0045] A polymer according to Example 1 was prepared and processed in a plant according to Figure 2. The reaction mixture was separated into two phases by reducing the pressure to 1.5×10^7 Pa (150 bar) in the separator A. A phase (I) polymer/sc fluid and a phase (II) monomer/sc fluid was obtained. Phase (II) which was enriched with monomers, was drawn off. Phase (I) was conveyed with a pump P1 to the static mixer M. An anhydride hardener was melted at a temperature of 120°C in the preparation vessel V2. The melt of the hardener was conveyed to the static mixer with a pump P2. The pumps P1 and P2 were adjusted such that the mass flow ratio of polymer/hardener in the static mixer was 80/20. In addition, e-sc fluid in a mass ratio of 1:1 (based on mass of polymer plus mass of hardener) was conveyed from vessel V 1 to the static mixer with a diaphragm compressor P3. The sc fluid was heated to 120°C in the heat exchanger W. The mass flows were intensively mixed in the static mixer at 120°C and 150 bar and the melt mixture containing CO_2 was depressurised with a hollow cone nozzle (bore 0.7 mm diameter, spray cone 90°) and a powder coating was obtained. A temperature of 42°C was obtained in the spray tower S at a pressure of about 1 bar. The residual monomers contained in the polymer mixture were evaporated and drawn off together with the sc fluid with an exhaustor P4. Entrained powder coating was separated from the sc fluid using a cyclone Z.

Example 4

[0046] A polymer according to Example 1 was prepared and processed in a plant according to Figure 3. The reaction mixture was transferred to an extraction column E whilst lowering the pressure to 1.5×10^7 Pa (150 bar). Monomers were removed from the polymer in the column at a pressure of 150 bar and a temperature

of 120°C by means of an sc fluid flowing in counter-current. At the top of the column the sc fluid was drawn off with the monomers dissolved therein. The sc fluid was separated from the monomers in the separator A by reducing the pressure to 5×10^6 Pa (50 bar). The purified sc fluid was compressed again by means of a compressor P5 and used again for extraction. At the bottom of the column E the polymer from which the monomers had been removed was drawn off and fed to a static mixer M by means of a pump P1. An anhydride hardener was melted at a temperature of 120 °C in the preparation vessel V2. The melt of the hardener was conveyed to the static mixer with a pump P2. The pumps P1 and P2 were adjusted such that the mass flow ratio of polymer/hardener in the static mixer was 80/20. In addition, sc fluid in a mass ratio of 1:1 (based on mass of polymer plus mass of hardener) was conveyed from vessel V1 to the static mixer with a diaphragm compressor P3. The sc fluid was heated to 120°C in the heat exchanger W. The mass flows were intensively mixed in the static mixer at 120°C and 1.5×10^7 Pa (150 bar) and the melt mixture containing CO₂ was depressurised with a hollow cone nozzle (bore 0.7 mm diameter, spray cone 90°) and a powder coating was formed. A temperature of about 40°C was obtained in the spray tower S at a pressure of 10^5 Pa (1 bar). The sc fluid was drawn off with an exhaustor P4. Further powder coating was separated from the sc fluid using a cyclone Z.

Claims

1. A process for the preparation of polymers in supercritical (sc) fluids as reaction medium from at least two copolymerisable ethylenically unsaturated monomers and conventional initiators and regulators, **characterised in that**
 - the monomers, initiators and regulators are mixed with the sc fluid to give a mixture with a sc fluid content up to 37,5 wt.-% before initiating the polymerisation,
 - the reaction is carried out in the homogeneous phase,
 - after the reaction has ended, the phase parameters pressure and or temperature are altered so that at least two phases are formed, a phase I containing predominantly polymer and sc fluid and the other phase II containing predominantly unreacted monomers and sc fluid, wherein, without departing from the sc phase conditions,
 - phase I is separated and
 - the polymer from phase I is converted to a polymer powder by depressurising and removing the sc fluid.
2. A process according to claim 1, wherein the content of the sc fluid is up to 25 wt.-% before initiating the

polymerisation.

3. A process according to claim 1 and 2, **characterised in that** non reactive supercritical solvents are used as sc fluid.
4. A process according to claim 1 to 3, **characterised in that** at least three copolymerisable ethylenically unsaturated monomers are used, at least one monomer containing a further functional group.
5. A process according to claim 4 **characterised in that** styrene, methylmethacrylate, isobornylmethacrylate and glycidylmethacrylate are used.
6. A process according to claim 1 to 5, **characterised in that** up to 20 wt-% of an organic solvent is added to the supercritical fluid.
7. A process according to claim 1 to 6 **characterised in that** the pressure is from 80 to 450 bar and the temperature is from 70 to 250°C.
8. A process according to claim 1 to 7, **characterised in that** the reaction is carried out batchwise.
9. A process according to claim 1 to 7, **characterised in that** the process is carried out continuously.
10. A process according to claim 8 and 9, **characterised in that** volatile accompanying substances are separated from the resulting polymer powder when the sc fluid is depressurised.
11. A process according to claim 8 and 9, **characterised in that**, prior to depressurisation, phase I is purified with a further separation step, preferably in a counter-current extraction process using an sc fluid.
12. A process according to claim 1, **characterised in that** phase II is separated and recycled to the polymerisation process.
13. A process according to claim 12, **characterised in that** monomers and accompanying substances are separated from phase II before the sc fluid is recycled.
14. A process for the preparation of powder coatings, **characterised in that** the polymer powder is prepared in the homogeneous phase by reaction in the sc fluid according to a process according to claim 1,
 - the separated phase I optionally undergoes a further step for the separation of accompanying substances.
 - phase I is further processed directly by the ad-

- dition of further components of a powder coating, and
- the resulting process mixture is converted to a fine-particle solid powder coating by depressurising the sc fluid.
15. A process according to claim 14, **characterised in that** further components selected from the group consisting of hardeners, powder coating additives, dyes, pigments and extenders are used.
16. A process according to claim 14 and 15, **characterised in that** a hardener that reacts with the functional groups of the polymer is added as a further component.
17. A process according to claim 14 to 16, **characterised in that** further additives are added to the process mixture.
18. A process according to claim 17 wherein after addition of additives to the process mixture further sc fluid is added.
19. A process according to claim 14 to 17 **characterised in that** the added components, before being added and mixed, are homogenised in an identical or different sc fluid.
20. A process according to claim 14, **characterised in that** the process mixture is sprayed by means of a nozzle into a spray tower.
21. A process according to claim 14, **characterised in that** the process mixture is sprayed by means of a nozzle into a liquid, preferably aqueous medium.
22. A process according to claim 14 to 21 **characterised in that** the sc fluid which is gaseous after spraying is purified and recycled to the process.
23. Powder coating prepared by process according to claim 14, **characterised in that** the polymer comprises at least three copolymerisable ethylenically unsaturated monomers, at least one monomer additionally containing further reactive functional groups, the dispersity of the binder is < 3 , and contains further conventional binders, hardeners, auxiliaries and other additives.
24. Powder coating according to claim 23 **characterised in that** styrene, methylmethacrylate, isobornylmethacrylate and glycidylmethacrylate are used.
25. Powder coating according to claim 23, **characterised in that** the average particle size is below 50 μm .

26. Powder coating according to claim 23, **characterised in that** the powder coating is a powder clear coat.
27. Powder coating according to claim 23, **characterised in that** the powder coating is coloured with pigments and/or dyes.
28. The use of a powder coating according to claim 14 and 26 or 27 for use in multi-layer coating.
29. The use according to claim 28 in the automotive industry.

Patentansprüche

1. Verfahren zur Herstellung von Polymeren in superkritischen (sc) Fluiden als Reaktionsmedium aus mindestens zwei copolymerisierbaren, ethylenisch ungesättigten Monomeren und konventionellen Initiatoren und Reglersubstanzen, **dadurch gekennzeichnet, dass:**
 - die Monomere, Initiatoren und Reglersubstanzen mit dem sc-Fluid gemischt werden, um eine Mischung mit einem Gehalt an sc-Fluid bis zu 37,5 Gew.% zu ergeben, bevor die Polymerisation initiiert wird;
 - die Reaktion in der homogenen Phase ausgeführt wird;
 - nach dem Ende der Reaktion die Phasenparameter Druck und/oder Temperatur derart verändert werden, dass mindestens zwei Phasen gebildet werden, wobei Phase I überwiegend Polymer und sc-Fluid enthält und die andere Phase II überwiegend nicht umgesetzte Monomere und sc-Fluid enthält; in welchem Verfahren, ohne von den sc-Phasenbedingungen abzuweichen:
 - Phase I abgetrennt wird und
 - das Polymer von Phase I umgewandelt wird zu einem Polymerpulver durch Drucklosmachen und Entfernen des sc-Fluid.
2. Verfahren nach Anspruch 1, worin vor dem Initiieren der Polymerisation der Gehalt an sc-Fluid bis zu 25 Gew.% beträgt.
3. Verfahren nach Anspruch 1 und 2, **dadurch gekennzeichnet, dass** als sc-Fluid nichtreaktionsfähige, superkritische Lösemittel verwendet werden.
4. Verfahren nach Anspruch 1 bis 3, **dadurch gekennzeichnet, dass** mindestens drei copolymerisierbare, ethylenisch ungesättigte Monomere verwendet werden und mindestens ein Monomer eine

weitere funktionelle Gruppe enthält.

5. Verfahren nach Anspruch 4, **dadurch gekennzeichnet, dass** Styrol, Methylmethacrylat, Isobornylmethacrylat und Glycidylmethacrylat verwendet werden.
6. Verfahren nach Anspruch 1 bis 5, **dadurch gekennzeichnet, dass** dem superkritischen Fluid bis zu 20 Gew.% eines organischen Lösemittels zugesetzt werden.
7. Verfahren nach Anspruch 1 bis 6, **dadurch gekennzeichnet, dass** der Druck 80 bis 450 Bar und die Temperatur 70° bis 250°C betragen.
8. Verfahren nach Anspruch 1 bis 7, **dadurch gekennzeichnet, dass** die Reaktion chargenweise ausgeführt wird.
9. Verfahren nach Anspruch 1 bis 7, **dadurch gekennzeichnet, dass** der Prozess kontinuierlich ausgeführt wird.
10. Verfahren nach Anspruch 8 und 9, **dadurch gekennzeichnet, dass** aus dem resultierenden Polymerpulver flüchtige Begleitsubstanzen abgetrennt werden, wenn das sc-Fluid drucklos gemacht wird.
11. Verfahren nach Anspruch 8 und 9, **dadurch gekennzeichnet, dass** vor dem Drucklosmachen Phase I mit einem weiteren Trennschritt gereinigt wird und bevorzugt in einem Verfahren der Gegenstromextraktion unter Verwendung eines sc-Fluids.
12. Verfahren nach Anspruch 1, **dadurch gekennzeichnet, dass** Phase II abgetrennt wird und in den Kreislauf des Polymerisationsprozesses zurückgeführt wird.
13. Verfahren nach Anspruch 12, **dadurch gekennzeichnet, dass** Monomere und Begleitsubstanzen aus Phase II abgetrennt werden, bevor das sc-Fluid in den Kreislauf zurückgeführt wird.
14. Verfahren zur Herstellung von Pulverbeschichtungen, **dadurch gekennzeichnet, dass** das Polymerpulver in der homogenen Phase durch Reaktion in dem sc-Fluid nach einem Verfahren nach Anspruch 1 abgetrennt wird, wobei
 - die abgetrennte Phase I wahlweise einem weiteren Schritt für die Abtrennung von Begleitsubstanzen unterworfen wird,
 - Phase I durch Zugabe von weiteren Komponenten einer Pulverbeschichtung direkt weiterverarbeitet wird,
 - das resultierende Prozessgemisch durch

Drucklosmachen des sc-Fluids zu einer feinteiligen, festen Pulverbeschichtung umgewandelt wird.

- 5 15. Verfahren nach Anspruch 14, **dadurch gekennzeichnet, dass** weitere Komponenten verwendet werden, die ausgewählt sind aus der Gruppe, bestehend aus: Härtern, Additiven für die Pulverbeschichtung, Farbstoffen, Pigmenten und Verschnittmitteln.
- 10 16. Verfahren nach Anspruch 14 und 15, **dadurch gekennzeichnet, dass** ein Härter, der mit den funktionellen Gruppen des Polymers reagiert, als eine weitere Komponente zugesetzt wird.
- 15 17. Verfahren nach Anspruch 14 bis 16, **dadurch gekennzeichnet, dass** dem Prozessgemisch weitere Additive zugesetzt werden.
- 20 18. Verfahren nach Anspruch 17, **dadurch gekennzeichnet, dass** nach Zugabe von Additiven zu dem Prozessgemisch weiteres sc-Fluid zugesetzt wird.
- 25 19. Verfahren nach Anspruch 14 bis 17, **dadurch gekennzeichnet, dass** die zuzusetzenden Komponenten, bevor sie zugesetzt und gemischt werden, in einem identischen oder anderem sc-Fluid homogenisiert werden.
- 30 20. Verfahren nach Anspruch 14, **dadurch gekennzeichnet, dass** das Prozessgemisch mit Hilfe einer Düse in einen Sprühturm gespritzt wird.
- 35 21. Verfahren nach Anspruch 14, **dadurch gekennzeichnet, dass** das Prozessgemisch mit Hilfe einer Düse in eine Flüssigkeit und bevorzugt ein wässriges Medium gespritzt wird.
- 40 22. Verfahren nach Anspruch 14 bis 21, **dadurch gekennzeichnet, dass** das sc-Fluid, das nach dem Sprühen gasförmig ist, gereinigt wird und in den Kreislauf des Prozesses zurückgeführt wird.
- 45 23. Pulverbeschichtung, hergestellt nach dem Verfahren nach Anspruch 14, **dadurch gekennzeichnet, dass** Polymer mindestens drei copolymerisierbare, ethylenisch ungesättigte Monomere aufweist und mindestens ein Monomer, das zusätzlich weitere funktionelle Gruppen enthält, der Dispersionsgrad des Bindemittels < 3 beträgt und weitere konventionelle Bindemittel, Härter, Hilfsstoffe und andere Additive enthalten sind.
- 50 24. Pulverbeschichtung nach Anspruch 23, **dadurch gekennzeichnet, dass** Styrol, Methylmethacrylat, Isobornylmethacrylat und Glycidylmethacrylat verwendet werden.
- 55

25. Pulverbeschichtung nach Anspruch 23, **dadurch gekennzeichnet, dass** die mittlere Partikelgröße kleiner ist als 50 Mikrometer.
26. Pulverbeschichtung nach Anspruch 23, **dadurch gekennzeichnet, dass** die Pulverbeschichtung ein Pulverklarlack ist.
27. Pulverbeschichtung nach Anspruch 23, **dadurch gekennzeichnet, dass** die Pulverbeschichtung mit Pigmenten und/oder Farbstoffen farbig ist.
28. Verwendung einer Pulverbeschichtung nach Anspruch 14 und 26 oder 27 zur Verwendung in mehrlagigen Beschichtungen.
29. Verwendung nach Anspruch 28 in der Automobilindustrie.

Revendications

1. Procédé pour la préparation de polymères dans des fluides supercritiques (sc) en tant que milieu de réaction à partir d'au moins deux monomères éthyléniquement insaturés copolymérisables et d'initiateurs et régulateurs classiques, **caractérisé en ce que**
- les monomères, initiateurs et régulateurs sont mélangés avec le fluide sc pour donner un mélange ayant une teneur en fluide sc allant jusqu'à 37,5% en poids avant de déclencher la polymérisation,
 - la réaction est effectuée en phase homogène,
 - au terme de la réaction, les paramètres de pression et/ou température des phases sont modifiés de sorte qu'au moins deux phases sont formées, une phase I contenant principalement le polymère et le fluide sc et l'autre phase II contenant principalement les monomères non réagis et le fluide sc, et sans s'éloigner des conditions de phase sc,
 - la phase I est séparée et
 - le polymère de la phase I est converti en une poudre de polymère en dépressurant et en éliminant le fluide sc.
2. Procédé selon la revendication 1, dans lequel la teneur en fluide sc va jusqu'à 25% en poids avant de déclencher la polymérisation.
3. Procédé selon les revendications 1 et 2, **caractérisé en ce que** des solvants supercritiques non réactifs sont utilisés en tant que fluide sc.
4. Procédé selon les revendications 1 à 3, **caractérisé en ce qu'**au moins trois monomères éthylénique-

ment insaturés copolymérisables sont utilisés, au moins un monomère contenant un autre groupe fonctionnel.

5. Procédé selon la revendication 4, **caractérisé en ce que** du styrène, du méthacrylate de méthyle, du méthacrylate d'isobomyle et du méthacrylate de glycidyle sont utilisés.
6. Procédé selon les revendications 1 à 5, **caractérisé en ce que** jusqu'à 20% en poids d'un solvant organique est ajouté au fluide supercritique.
7. Procédé selon les revendications 1 à 6, **caractérisé en ce que** la pression va de 80 à 450 bars et la température va de 70 à 250°C.
8. Procédé selon les revendications 1 à 7, **caractérisé en ce que** la réaction est effectuée de façon discontinue.
9. Procédé selon les revendications 1 à 7, **caractérisé en ce que** le procédé est mis en oeuvre de façon continue.
10. Procédé selon les revendications 8 et 9, **caractérisé en ce que** les substances volatiles d'accompagnement sont séparées de la poudre de polymère obtenue lorsque le fluide sc est dépressurisé.
11. Procédé selon les revendications 8 et 9, **caractérisé en ce que**, avant la dépressurisation, la phase I est purifiée avec une étape de séparation supplémentaire, de préférence dans un procédé d'extraction à contre-courant en utilisant un fluide sc.
12. Procédé selon la revendication 1, **caractérisé en ce que** la phase II est séparée et recyclée au traitement de polymérisation.
13. Procédé selon la revendication 12, **caractérisé en ce que** les monomères et les substances d'accompagnement sont séparées de la phase II avant de recycler le fluide sc.
14. Procédé pour la préparation de revêtements de poudre, **caractérisé en ce que** la poudre de polymère est préparée en phase homogène par réaction dans le fluide sc d'après un procédé selon la revendication 1,
- la phase I séparée subit facultativement une autre étape pour séparer les substances d'accompagnement,
 - la phase I est ensuite traitée directement par l'addition des autres constituants d'un revêtement de poudre, et
 - le mélange de traitement obtenu est converti

en un revêtement de poudre solide à particules fines en dépressurant le fluide sc.

15. Procédé selon la revendication 14, **caractérisé en ce que** d'autres constituants choisis dans le groupe constitué par les durcisseurs, les additifs pour revêtement de poudre, les colorants, les pigments et les allonges sont utilisés.
16. Procédé selon les revendications 14 et 15, **caractérisé en ce que** un durcisseur qui réagit avec les groupes fonctionnels du polymère est ajouté en tant que constituant supplémentaire.
17. Procédé selon les revendications 14 à 16, **caractérisé en ce que** d'autres additifs sont ajoutés au mélange de traitement.
18. Procédé selon la revendication 17, dans lequel, après l'addition des additifs au mélange de traitement, du fluide sc supplémentaire est ajouté.
19. Procédé selon les revendications 14 à 17, **caractérisé en ce que** les constituants ajoutés, avant d'être ajoutés et mélangés, sont homogénéisés dans un fluide sc identique ou différent.
20. Procédé selon la revendication 14, **caractérisé en ce que** le mélange de traitement est pulvérisé au moyen d'une buse dans une tour de pulvérisation.
21. Procédé selon la revendication 14, **caractérisé en ce que** le mélange de traitement est pulvérisé au moyen d'une buse dans un milieu liquide, de préférence aqueux.
22. Procédé selon les revendications 14 à 21, **caractérisé en ce que** le fluide sc qui est gazeux après la pulvérisation est purifié et recyclé au procédé.
23. Revêtement de poudre préparé par le procédé selon la revendication 14, **caractérisé en ce que** le polymère comprend au moins trois monomères éthyléniquement insaturés copolymérisables, au moins un monomère contenant de plus d'autres groupes fonctionnels réactifs, la dispersité du liant est <3, et contient d'autres liants, durcisseurs, agents auxiliaires et autres additifs classiques.
24. Revêtement de poudre selon la revendication 23, **caractérisé en ce que** du styrène, du méthacrylate de méthyle, du méthacrylate d'isobornyle et du méthacrylate de glycidyle sont utilisés.
25. Revêtement de poudre selon la revendication 23, **caractérisé en ce que** la taille moyenne de particule est inférieure à 50µm.

26. Revêtement de poudre selon la revendication 23, **caractérisé en ce que** le revêtement de poudre est une couche de poudre transparente.

27. Revêtement de poudre selon la revendication 23, **caractérisé en ce que** le revêtement de poudre est coloré avec des pigments et/ou des colorants.

28. Utilisation d'un revêtement de poudre selon les revendications 14 et 26 ou 27 pour l'utilisation dans un revêtement multicouche.

29. Utilisation selon la revendication 28 en industrie automobile.

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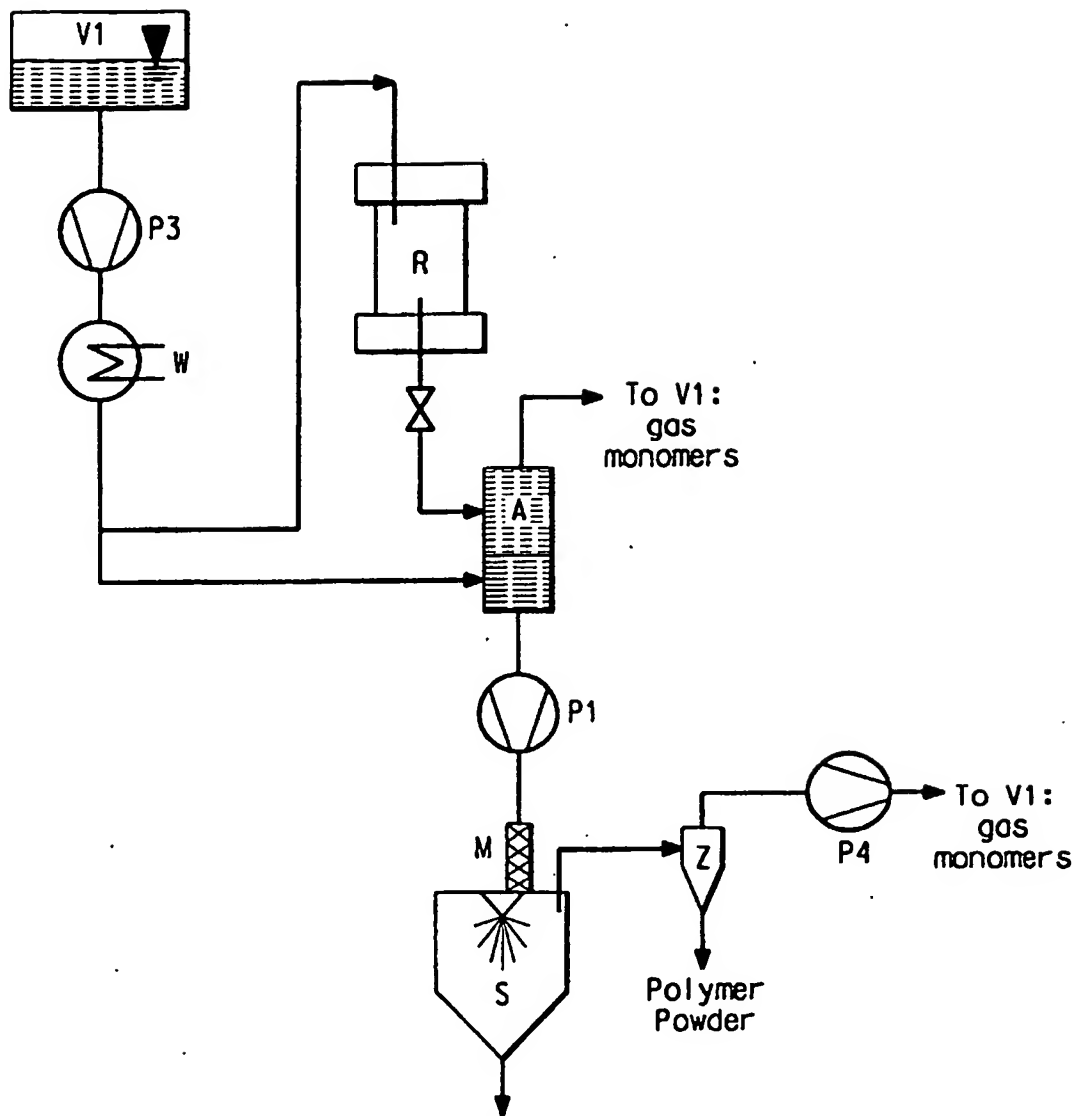


FIG. 1

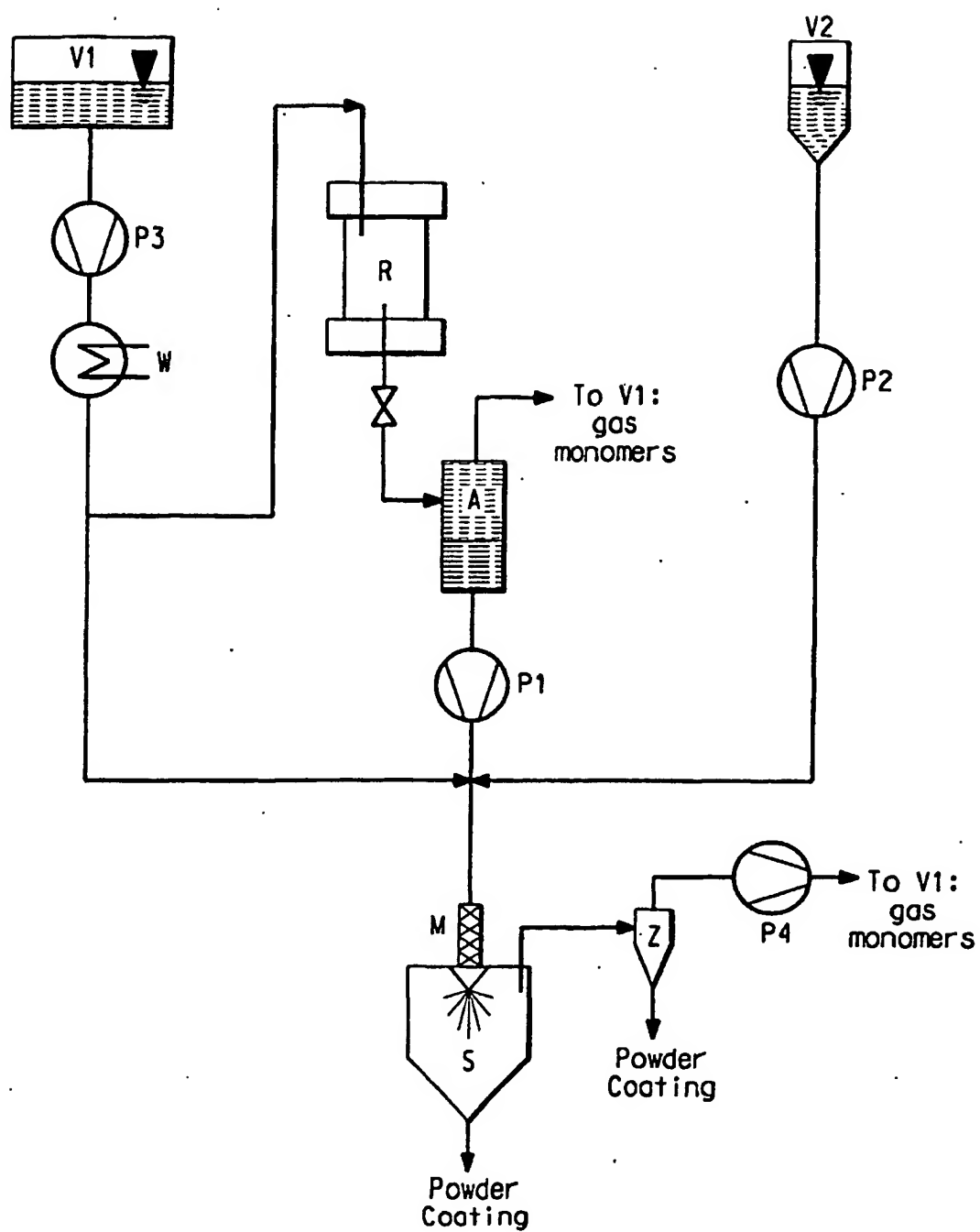


FIG. 2

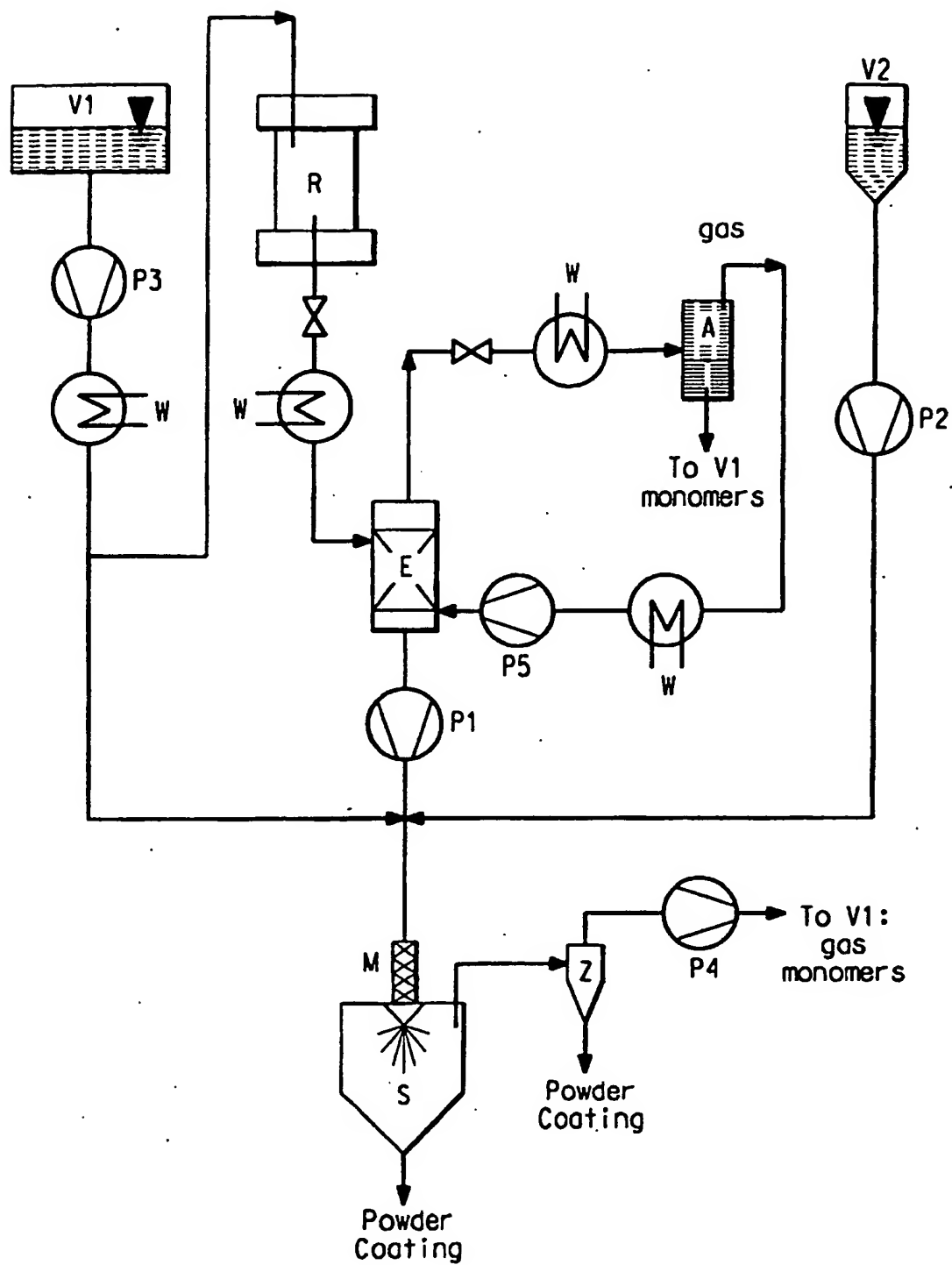


FIG. 3